Macromolecular and Chemical Changes Induced by Air-Oxidation of a Medium Volatile Bituminous Coal

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INTRODUCTION

The heterogeneity of coal, together with its complex macromolecular nature, has been responsible for much of the difficulties in elucidating its structure and chemical characterization. Most methods of investigation of the chemical structure and physical properties involve breaking macromolecules into smaller fragments by depolymerization, oxidation, reduction, dehydrogenation, acetylation, etc., which, for the most part, solubilizes a major fraction of the coal while trying to preserve as much of its original structure as possible. Depending upon the rank of coal and the solvent used, more than 80% of some coals have been solubilized.

Efforts have been made to study the macromolecular structure of coal as a complete entity with special emphasis on cross-linkages. Techniques are limited but swelling and Differential Mechanical Thermal Analysis (DMTA) have proved to be powerful tools in this important area. Although analyses of chemical fragments and macromolecular studies can give complementary information, neither approach alone can lead to final conclusions. No attempt is reported in the literature to simultaneously undertake both solubilization and macromolecular analyses. This paper reports the results of such an attempt. Air oxidation was chosen to modify the coal structure for several reasons.

Elliott (1) reviews the contributions made to the understanding of coal chemistry by researchers using destructive oxidation to reduce the macromolecular structure of coal to entities that can be explored with available instrumentation and known analytical procedures. Since air causes the natural oxidation of coal and because there is little chance that any atoms other than oxygen can be introduced into the coal molecule when it is used as the oxidant, only air was used for the oxidations in this study. The experiments were carried out at 200°C because no weight loss was observable upon heating in nitrogen at or below that temperature.

There have been many studies undertaken to determine the extent of cross-linking in the coal structure (2, 3). Most investigators believe that the more highly cross-linked the coal structure is, the less it will swell when contacted with an organic solvent. Liotta (4), using tetrahydrofuran on weathered coal, showed that swelling decreased as the time of weathering increased. However, if the nature of the cross-links are such that hydrogen bonds are responsible for much of the cross-linking, then work by Hall, et al., (2) suggests that attack by a basic solvent may result in an increase in swelling.

The problem of understanding the structure of coal is a complex one. It must be remembered that different coals react differently to reagents. The results that are reported in this paper may be applicable to other coals of similar rank and even coals of different ranks, but no such assumption is made in this study.

It is the purpose of this paper to not only provide researchers with additional insight into the macromolecular structure of coal and its chemical characterization, but also to demonstrate that a concerted effort using a variety of techniques on coal and its oxidation products, can make an important contribution to coal science.

EXPERIMENTAL

Coal Characteristics

The coal sample used in this investigation was a Cortonwood coal from the Silkstone seam furnished by British Coal (NCB Coal Rank Code 501, ISO Classification 634) ground to µm size. Important characteristics of the coal are summarized in Table 1.

Coal Oxidation

The coal was oxidized in air for one, two, four and six day periods at 200°C in a forced circulation oven.

Humic Acid Preparations

Water-insoluble samples of the oxidized coal were extracted with 0.1 M NaOH and precipitated with 0.1 M HCl. Centrifugation at 3500 rpm was used along with filtration to speed the recovery of the humic acids. Considerable washing with distilled water removes any NaCl or HCl absorbed on the humic acids. The humic acids were dried at 105°C.

Infrared Spectra of Coals

All spectra were recorded on a Nicolet 205 SXB FTIR spectrometer using KBr pellets. All samples submitted were dried at 105°C.

Volumetric Swelling Technique

The technique perfected by Green, et al., (5) of the procedure developed by Liotta, et al., (4) for measuring swelling was used. In this technique, µm coal samples were centrifuged at 3500 rpm in 6 mm tubes to ensure tight packing. The height of the coal column was measured to ±0.01 mm using a cathetometer. Excess solvent was added. The ground glass stoppered tubes were shaken every 12 hours until equilibrium was reached. Constant height readings of the coal column indicated equilibrium. After equilibrium, the tubes were again centrifuged and the height of the coal column measured. The swelling ratio, Q, is equal to the height of the swollen coal divided by the height of the unswollen coal. Reproducibility was found to be ±0.05 which is in agreement with that of Green (5) and Hall (2). To examine the structure of the coal hydrogen bonding and how it changes on oxidation, swelling was carried out in a set of sterically similar substituted pyridines of differing basicity. Hall, et al., (2) have shown that the weaker bases swell coals by dissociating weak hydrogen bonds from the macromolecular network while the stronger bases swell coals by dissociating stronger bonds from the structure. A plot of coal swelling (Q) against the pKb of the solvents gives an indication of the hydrogen bond energy distribution of the coal.

Thermal Gravimetric Analyses

A Stanton Redcroft STA-780 Series Thermal Analyser was used for thermal gravimetric analyses. Sample masses of 12-26 mg was used, with heating rates of approximately 6°C to 20°C min^{-1} in nitrogen at temperatures from room temperature to 1000°C.

Petrographic Techniques

Reflectance was measured at 546 nm using oil immersion objectives (n=1.518 at 23°C) on a Leitz MPV3 Microscope Photometer. The photocathode was an EMI S-11. The samples were mounted in epoxy resins and were ground and polished according to the procedures prescribed by Stach, et al., (6). Twenty-five measurements were recorded for each sample in polarized light.

Results and Discussional

Humic Acid Formation

A series of experiments were carried out to determine the rate of oxidation in terms of humic acid formation as a function of time of oxidation. Table 2 and Figure 1 shows the yields of humic acid formation versus time of oxidation while Figure 2 shows a plot of the rate of humic acid production versus time of oxidation. From Figure 2, the maximum rate of humic acid formation should occur at 2.33 days. Of the four periods of oxidation used in these experiments, oxidation for two days showed the maximum yield.

The nature of the humic acids obtained from each of the samples oxidized for various lengths of time showed no functional group differences--as evidenced by infrared analyses. The spectra were characterized by the very broad bands covering C-H and O-H stretching frequencies at the 2500 cm^{-1} to 3500 cm^{-1} region; the COO- absorption at 1709 cm^{-1}; aromatic and/or hydrogen bonded carbonyls at 1604 and 1216 cm^{-1}; and the shoulder at 1376 cm^{-1} usually assigned to phenolic O–H.

Upon petrographic examination, the humic acids appeared to be isotropic with a random orientation as evidenced when inserted in cross polars with a full wave length retarder plate. The colours were invariant purple during rotation of the stage. The reflectivity did not change on stage rotation using plane polarized light. No pyrite was visible in the humic acids. Large curved cracks from swelling and shrinking were evident. The surface was rather soft, probably due to the sample being polished with relief. The reflectivity was lower than the coal, in the 0.85 range. No visible fluorescence was noticed under ultra violet excitation. To the naked eye, the humic acids appeared to be a black, crystalline solid.

Because of the relative non-volatility of the coal as well as the humic acids, mass spectrometry did not provide useful data in this investigation. Instrument limitations prevented analyses beyond 300°C and thermal gravimetric analyses demonstrated that there was little or no weight loss of the coal below 400°C.

The oxidized coal residue, resulting after the humic acids were extracted, emitted a yellow-brown fluorescence under ultraviolet and blue wavelength excitation during observations made when using fluorescence microscopy indicating the presence of aliphatic hydrocarbons. A considerable amount of pyrite was visible when viewed under polarized light in various states of preservation, ranging from pristine to a severely oxidized orange state. It appeared that 25-30% of the residue of the sample that was oxidized for six days was pyrite. Byers (7) presents an in-depth discussion of the problems caused by pyrites in coal during furnace operation. Although washing and float and sink methods have had some success in removing pyrites from many coals, small particles usually get into the furnace resulting in high sulphur emissions, slagging and furnace problems. Air oxidation at relatively low temperature followed by an alkaline wash may enhance pyrite removal from coal.

Swelling as a Result of Oxidation

In the experiments carried out in this study, evidence is presented to indicate that basic organic solvents can effect cross-linkages caused by oxidation because of the formation and destruction of hydrogen bonds.

The effect of oxidation on the hydrogen bond structure can be interpreted from Figure 3. There is an initial increase in swelling from the fresh coal to the one day oxidized coal suggesting an initial increase in all strengths of hydrogen bonding. Oxidation from one to two days reduces swelling in the weaker bases (pKb<8) but increases swelling in the strongest base. This suggests that weak hydrogen bonds are being eliminated from the structure and hydrogen bonds are being formed that are not susceptible to attack by pyridine. Further oxidation does not change the density of weak hydrogen bonds to any great extent but swelling in the two strongest bases increases, which implies an increase in the density of strong hydrogen bonds in the structure.

When this data is coupled with the increase of humic acid yield on oxidation the implication is that initial oxidation (up to two days) attacks the alkane and cycloalkane groups, changing these into hydrogen bond crosslinks which are relatively weak and can be broken by the weaker bases. Further oxidation (after two days) is associated with significant production of humic acids. Humic acids have large concentrations of carboxylic acid groups and such groups may lead to strong hydrogen bonding in the coal matrix.

Infrared studies appear to support the data obtained from swelling studies. The oxidation of the coal to form humic acids appears to be due in part to the oxidation of aliphatic groups. The intensity of the alkyl group band at 2900 cm^{-1} is diminished considerably after one day of oxidation. Under petrographic study, increases in the vitrinite reflectance along with increased reflectance of the exinite may be due to increased aromaticity as the coal is progressively oxidized for one and two days. After two days, further oxidation decreases the reflectance indicating the possible attack on aromatic structure. Table 3 shows the reflectance data for the unoxidized and oxidized coals and Figure 4 shows the plot of the data. Figure 5 shows the histograms. Thus it appears that initial oxidation attacks both the alkane and cycloalkane structure of the coal, some of which act as cross-linkages to aromatic clusters. The Cortonwood coal has a relatively high H/C ratio when compared to most medium volatile bituminous coals. The strong hydrogen bonds appear to be associated with the high density of carboxylic acids that are present in the humic acids. The infrared spectra of the unoxidized and oxidized coals show a strong band formed at 3418 cm^{-1} and another strong band at approximately 1700 cm^{-1} appearing after oxidation for one day indicating humic acid formation. The 3418 cm^{-1} band is characteristic of strongly hydrogen bonded OH groups (8) and the 1700 cm^{-1} peak is characteristic of COO^- formation (9, 10, 11, 12). The intensity of the alkyl band at 2900 cm^{-1} present in the spectra of the original coal is diminished considerably after one day of oxidation.

Using thermal gravimetric analyses, it can be demonstrated that the weight loss upon heating the unoxidized Cortonwood coal in nitrogen from 105°C to 200°C and maintaining the sample at 200°C for five minutes resulted in no weight loss. It is interesting to note that no appreciable weight loss occurred when pyrolysing the coal under nitrogen until over 400°C. Only about 32% of the coal is ever volatilized at temperatures up to 950°C. Figure 6 shows the results of the thermal gravimetric analyses of the unoxidized coal. The sample lost less then 1.9% moisture upon heating from room temperature to 105°C.

SUMMARY

Air oxidation of a medium volatile bituminous coal at 200°C for six days yields 85% by weight humic acids. The rate of oxidation increases to a maximum at 2.33 days and decreases in a Gausian distribution. The humic acids are characterized by their infrared spectra showing a strong band at 1709 cm^{-1} for the COO^- group, the strong band at 1604 and 1216 cm^{-1} indicative of aromatic and/or hydrogen bonded carbonyl, and a shoulder at 1376 cm^{-1} usually assigned to phenolic OH. Oxidation of coal results in the formation and destruction of hydrogen bonds. Hydrogen bonds form as humic acids are produced from the oxidation of alkyl and alicyclic cross-linkages in the macromolecular structure. Weak hydrogen bonds, already existing in the coal and formed during the oxidation are attacked by pyridine and lead to swelling. Substituted pyridines having pK_b values higher than pyridine are able to break stronger hydrogen bonds in the oxidized coals. Petrographic studies and thermal gravimetric analyses support the information generated by the data gathered from swelling experiments and infrared absorption investigation.

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REFERENCES

1. Elliott, M.A., "Chemistry of Coal Utilization", John Wiley & Sons, 1981, p. 455-469.
2. Hall, P.J., Marsh, H. and Thomas, M.K., submitted to Fuel.
3. Korov, N.Y., O'Shea, J.M. and Sergeant, G.D., Fuel, 1967, 46, 415.
4. Liotta, R., Brown, G. and Isaacs, J., Fuel, 1984, 63, 935.
5. Green, T.K., Kovac, J. and Larson, J.W., Fuel, 1984, 63, 935.
6. Stack, E., Mackowsky, M-Th., Teichmuller, N., Taylor, G.H., Chandra, D., and Teichmuller, R., "Stack's Textbook of Coal Petrology", Gebruder Borutraeger, 1982, p. 295.
7. Byers, R.W., "The Physical and Chemical Characteristics of Pyrites and Their Influence on Fireside Problems in Steam Generators", ASME Paper No. 75-WA/CD-2, 1975.
8. Silverstein, R.M., Bossler, G.C., and Morrill, T.C., "Spectrometric Identification of Organic Compounds", 3rd Edition, John Wiley & Sons, 1974, p. 91.
9. Painter, P.C., Snyder, R.W., Pearson, D.E. and Kwong, J., Fuel, 1980, 59, 282.
10. Chang, K.K., Flagan, R.C., Gavalas, G.R. and Sharma, P.K., Fuel 1986, 65, 75.
11. Rhoads, C.A., Senftle, J.T., Coleman, M.M., Davis, A. and Painter, P.C., Fuel, 1983, 62, 1387.
12. Starsinic, M., Otake, Y., Walker, P.L. and Painter, P.C., Fuel, 1984, 63, 1003.

Table 1
Characteristics of Cortonwood Coal

Proximate Analysis (as determined)	wt.%
Moisture	1.0
Ash	2.2
Volatile Matter	34.7
Fixed Carbon	62.1

Ultimate Analysis (dry mineral matter free basis)	
Carbon	87.20
Hydrogen	5.60
Oxygen (diff.)	3.9
Nitrogen	1.70
Sulphur	0.70

Table 2
Yield of Humic Acids

Time of Oxidation (days)	Yield of Humic Acids (%)
1	3.4
2	18.8
4	78.7
6	85.8

Table 3
Reflectance of Unoxidized and Oxidized Cortonwood Coal

Time of Oxidation (days)	Reflectance (% R_{mean})	Standard of Deviation
0	0.91	0.07
1	1.15	0.09
2	1.27	0.07
4	1.19	0.08
6	1.10	0.08

Figure 2. Rate of Humic Acid Production vs. Time

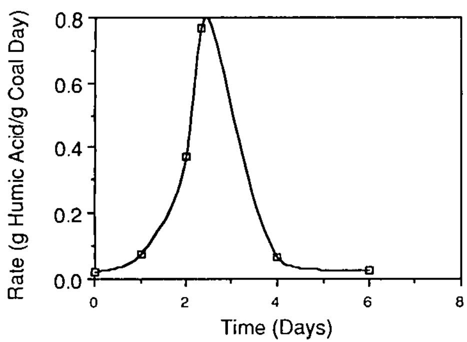

Figure 1. % Humic Acid Production vs. Time

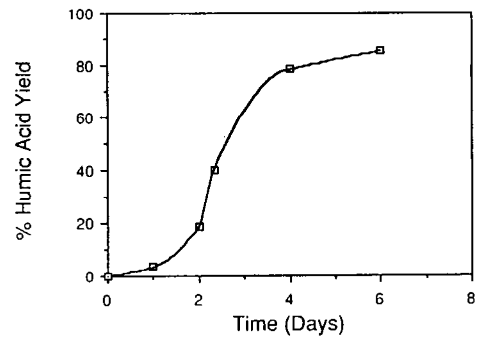

Figure 3. The Effect of Oxidation on Cortonwood Swelling

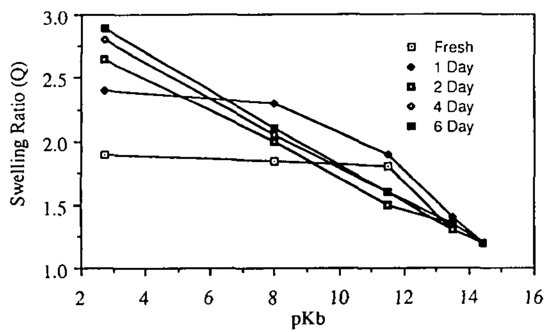

Figure 4. Reflectance vs. Time of Oxidation

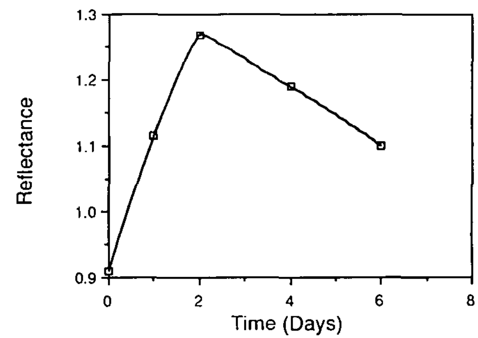

Figure 6. TGA of Cortonwood in Nitrogen

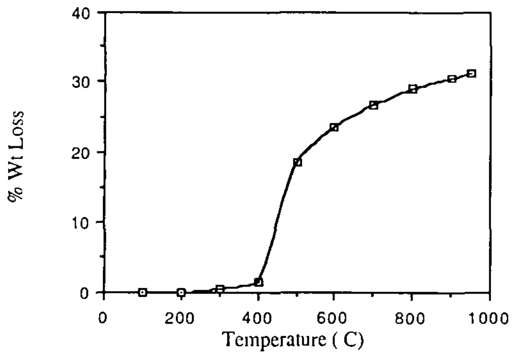

Figure 5. Reflectance Histogram of Unoxidized and Oxidized Cortonwood Coal